infrared and ^{1}H and ^{13}C NMR data for dimers described in this work, ^{2}H NMR spectra of perdeuterated and monodeuterated octatrienes, and 400-MHz ^{1}H NMR spectra of (*E,E*)-4,5-dimethyl-1,3,6-octatriene without and in the presence of Eu(tfc)$_3$ and Ag(fod) (5 pages). Ordering information is given on any current masthead page.

Dihydrogen Complexes of Metalloporphyrins: Characterization and Hydrogen-Transfer Reactivity

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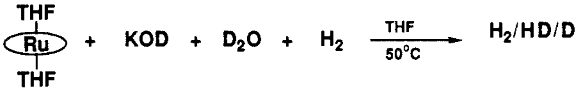
Extensive reports of η^2 coordination of dihydrogen to transition metals[2] have recently led to speculation that the η^2-dihydrogen complexes and their corresponding transition-metal hydrides may be important in the biological activation of molecular hydrogen.[3] We now report that protonation of transition-metal porphyrin hydrides has yielded the first known dihydrogen complex of a metalloporphyrin and a system that performs some functions of hydrogenase enzymes.[4]

The previously reported monohydrides,[5,6] K[M(OEP)(H)], M = Ru (**RuH**), Os (**OsH**), were prepared by potassium metal reduction of the corresponding dimers [M(OEP)]$_2$ in THF followed by protonation with excess water or *tert*-butyl chloride. The ^{1}H NMR spectrum shows that protonation of **OsH** with benzoic acid in THF affords in approximately 30% yield a porphyrinic product formulated as Os(OEP)(H$_2$), **OsH$_2$**.[7,8] In particular, the high-field singlet of **OsH$_2$** (δ −30.00)[9] is replaced by a triplet (δ −30.01, $^1J_{\mathrm{HD}}$ = 12 Hz) when Os(OEP)(HD), **OsHD**, is formed by the reaction of **OsH** with benzoic acid-d_1. The magnitude of this coupling and the minimum observed relaxation time (T_1 = 110 ± 8 ms for **OsH$_2$** at −20 °C in THF) suggest the presence of an η^2-dihydrogen ligand.[10,12] In addition, the methylene protons of the OEP ethyl substituents appear as a multiplet in the 400-MHz NMR spectrum, indicating that the two faces of the porphyrin are inequivalent[17] and precluding the presence of the *trans*-dihydride.

The above NMR parameters are consistent with formulation of **OsH$_2$** as a dihydrogen complex rather than a *cis*- or *trans*-dihydride. However, both $^1J_{\mathrm{HD}}$ and T_1 are near the limits proposed for formulation as η^2 coordination. The 12-Hz coupling constant is notably lower than that seen for most molecular hydrogen complexes in the literature (18 Hz < $^1J_{\mathrm{HD}}$ < 34 Hz),[2] although values as low as 13.7 Hz have been reported.[18] Additionally, T_1 is in the upper limit of the range acceptable for unambiguous classification as a molecular hydrogen complex. Together, these parameters suggest a weaker H–H interaction than found in most dihydrogen complexes. Because the H$_2$ binding mode is suggested to be dependent upon backbonding from the metal, dinitrogen stretching frequencies of L$_n$M(N$_2$) complexes (diagnostic of the extent of metal backbonding to the N$_2$ ligand) have been used to predict the stability and coordination mode of the corresponding L$_n$MH$_2$ complexes.[19] The ν(N$_2$) for Os(OEP)(THF)(N$_2$) is 2030 cm^{-1},[20] which is in the range where the corresponding H$_2$ complex, **OsH$_2$**, is expected to exist as a dihydride (<2060 cm^{-1}), and slightly below the range used to predict stable η^2-H$_2$ complexes (2060–2150 cm^{-1}). Such a ν(N$_2$) value reflects strong backbonding by the Os(II) center, a property conducive to increasing the dihydride character of the dihydrogen complex. The T_1, $^1J_{\mathrm{HD}}$, and ν(N$_2$) values are thus self-consistent and suggest that the electronic nature of Os(OEP) favors dihydride formation but that the rigid porphyrin constrains the H$_2$ to a single coordination site.

Since the dinitrogen stretching frequency for Ru(OEP)(THF)(N$_2$) is 2110 cm^{-1},[21] a dihydrogen complex of Ru(OEP) should have less dihydride character than the osmium analogue. Protonation of **RuH** with benzoic acid in THF results in rapid quantitative loss of dihydrogen to yield the bis solvato complex, Ru(OEP)(THF)$_2$, **Ru(THF)$_2$**. Such hydrogen loss is not surprising since Ru(II) is substitutionally more labile than Os(II). Even under 1 atm of H$_2$ in THF, **Ru(THF)$_2$**, known to be substitutionally labile,[22] does not form the proposed Ru(OEP)(H$_2$) in quantities observable by ^{1}H NMR.

Although we have been unable to observe Ru(OEP)(H$_2$) by NMR, its presence is suggested by the catalytic activity of **Ru(THF)$_2$** for H/D isotope exchange. A 10 mM solution of **Ru(THF)$_2$** in THF containing 12 equiv of KOD and 570 equiv of D$_2$O exchanges 6.9 equiv of deuterium between D$_2$O and H$_2$ gas when stirred at 50 °C under 0.13 atm of H$_2$ for 160 min[23] (eq 1). In



$$\mathrm{Ru(THF)_2} + \mathrm{KOD} + \mathrm{D_2O} + \mathrm{H_2} \xrightarrow[50^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{H_2/HD/D_2} \qquad (1)$$

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[6] Abbreviations: OEP = octaethylporphyrinato dianion; THF = tetrahydrofuran; NAD$^+$ = nicotinamide adenine dinucleotide (oxidized form).

[7] Os(OEP)(H$_2$): NMR (THF-d_8, 400 MHz) H$_{\mathrm{meso}}$ 9.29 (s), CH$_2$ 3.83 (m), CH$_3$ 1.81 (t), Os(H$_2$) −30.00 (s) ppm.

[8] The axial ligation of this species is unclear, though THF-d_8 is suspected.

[9] Transition-metal hydride resonances of porphyrins are shifted to very high field by the porphyrin ring current effect.[5] The hydride resonance of **OsH** before protonation to **OsH$_2$** is −65.6 ppm.

[10] $^1J_{\mathrm{HD}}$ for *cis*-dihydrides are typically <1 Hz,[11] 1 order of magnitude smaller than those typical of dihydrogen complexes.

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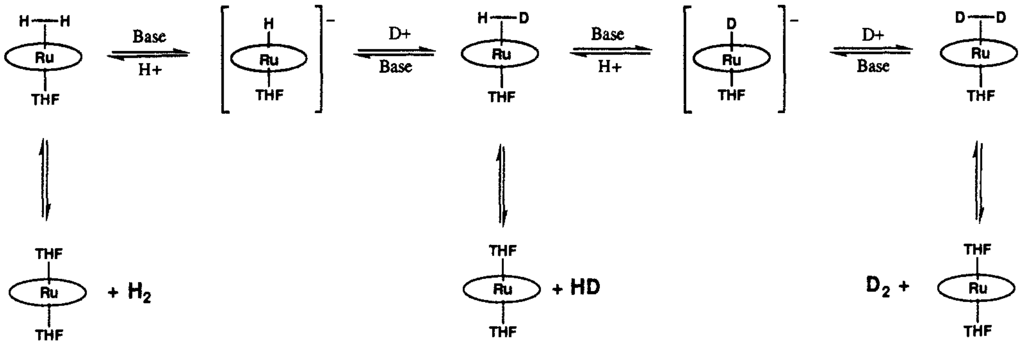
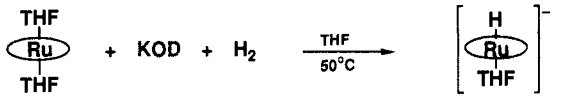
Scheme I



the absence of **Ru(THF)**$_2$, no measurable H/D exchange occurs. H/D exchange also does not occur in the absence of KOD. Additionally, this exchange is slowed by 30% when 120 equiv of KOD is added. Scheme I presents a mechanism we propose for this H/D exchange. The sequential acid-base equilibrium proposed in Scheme I has been independently shown to operate for the osmium analogue: e.g., **OsH**$_2$ is formed from protonation of **OsH** and is deprotonated by lithium diisopropylamide.[25] Also, **Ru(THF)**$_2$ forms the monohydride, **RuH**, when stirred in THF with KOD at 50 °C under 1 atm of H_2 (eq 2). The proposed



(2)

mechanism suggests that the rate of exchange should go through a maximum with pH since the overall process involves both a protonation and a deprotonation. This behavior is roughly exhibited with the above exchange results for **Ru(THF)**$_2$. Hydrogenase is also known to catalyze such H/D exchange and exhibits a similar pH profile.[26]

Because **RuH** forms from **Ru(THF)**$_2$ in the presence of H_2 and base, hydride transfer from **RuH** to a substrate may constitute a catalytic hydrogenation cycle involving **Ru(THF)**$_2$ as a catalyst. When a stoichiometric amount of the NAD^+ analogue (1-benzyl-*N*,*N*-diethylnicotinamide)PF_6 is introduced to an NMR solution of **RuH** in THF-d_8, a species with broad ^{1}H NMR resonances forms. Addition of a drop of pyridine to this mixture yields Ru(OEP)(py)$_2$ and the reduced nicotinamide, 1-benzyl-*N*,*N*-diethyl-1,6-dihydronicotinamide, as shown by the ^{1}H NMR. To our knowledge, this is the first example of a transition-metal hydride reducing an NAD^+ analogue.[27] This 1,6-addition contrasts with hydrogenase, which reduces NAD^+ at the 1,4-positions of the pyridinium.[4a] Further studies are planned to examine the selectivity of the NAD^+ reduction, to survey possible substrates for catalytic hydrogenation employing the **Ru(THF)**$_2$/H_2 system, and to further characterize dihydrogen complexes of transition-metal porphyrins.

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Free-Radical Carbonylation. Efficient Trapping of Carbon Monoxide by Carbon Radicals

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The reaction of carbon radicals with carbon monoxide to form acyl radicals[1,2] is thought to be an equilibrium process and to be difficult to control due to the ready back reaction.[3] In 1952, the formation of polyketones by peroxide-initiated copolymerization was first disclosed by Coffmann et al., who suggested the intermediacy of acyl radicals for this polymerization.[2a] In 1956, Foster et al. reported that the peroxide-initiated reaction of mercaptans with ethylene and carbon monoxide under 3000 atm at 130 °C gave 3-(alkylthio)propanal in 11–18% yields.[2c] While this reaction was noteworthy as a pioneering effort to effect trapping of acyl radicals by hydrogen abstraction, the results were of limited utility because of the extremely high pressures of CO and the low yields

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